

**THE FOLLOWING ARE THE ENGLISH TRANSLATION  
OF ANNEXES TO THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT (ARTICLE 34):**

Amended Sheets (Pages 1-4 & 18-20)

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Method for producing catalytically  
active layered silicates

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1

Description:

The invention relates to a method for producing catalytically active layered silicates with one or more intercalated layers, especially Al-pillared and/or Ti-pillared clays

Catalysts, especially denox catalysts, or in other words catalysts for removal of nitrogen oxides ( $\text{NO}_x$ ) in exhaust gases, are used on a large scale for exhaust-gas treatment in motor vehicles. In the case of catalytic post-combustion, the catalysts are composed of a support material with active coating and vibration-proof, thermally insulated bedding in a housing. Granules and monoliths of sintered  $\text{Al}_2\text{O}_3$  are used as support materials. The active catalyst layer is composed of small quantities of noble metals (Pt, Rh, Pd) and is known to be sensitive to lead.

Such motor-vehicle or even three-way or selective catalysts have proved themselves and are used to reduce NO to  $\text{NH}_3$  in a first step. After addition of secondary air, almost complete oxidation of CO and HC can then take place in a second step. In the process,  $\text{NH}_3$  is burned again to NO.

Such catalysts have been used for many years, but are not capable of being absolutely convincing from environmental and medical viewpoints. This has been shown only on the basis of recent vehicle studies on gasoline and diesel engines and is also reflected by traffic emission studies as well as current legislation. After all, the active catalyst layer of, for example, platinum (Pt) in such catalysts becomes detached in the course of time and is discharged into the surrounding air. Consequently, platinum accumulations have been observed in the human body, but the potential adverse effects are still unclear. In any case, a need exists to provide virtually emission-free catalysts.

Furthermore, it was reported only recently that toxic components are formed by reaction of carbon monoxide in platinum-base catalysts. These components may lead to cell mutations (see "Chemical and Engineering News", July 2002, page 8).

Certainly alternative catalyst concepts, such as those based on zeolites, have been discussed in the prior art. These zeolites were treated with transition metals. Here also, however, the formation of unhealthful secondary products, for example in the form of HCNO, has been observed. Moreover, the described catalysts do not have the requisite resistance to water, sulfur oxides and heavy metals.

In the prior art from which the present invention is derived, there is described the production of catalytically active layered silicates, also known as pillared clays, and of zeolite-type catalysts, wherein the charge-compensating cations in the intercalated layers of the respective layered silicates are replaced by larger inorganic hydroxymetal cations. This is achieved in a usually aqueous solution. Then the resulting substance is dried and calcined (see the paper of R.Q. Long and R.T. Yang, "The promoting role of rare earth oxides of Fe-exchanged  $\text{TiO}_2$ -pillared clay for selective catalytic reduction of nitric oxide by ammonia"; Applied Catalysis B: Environmental 27 (2000) 87-95). This is complex by virtue of the process sequence.

In the literature reference entitled "Preparation of acidic forms of montmorillonite clay via solid-state ion-exchange reactions" by M. Crocker et al. (Catalysis Letters 15 (1992) 339-345), the possibility is raised that ion exchange in the solid phase may be feasible in montmorillonite. For this purpose, a suitable metal nitrate is ground together with the clay in question at room temperature. In order to effect the ion exchange, two procedures in principle are suggested, namely an ultrasonic treatment and heating. Judging by the measured results, it appears that no ion exchange takes place during heating.

The technical problem underlying the invention is to provide a method for producing catalytically active layered silicates by means of which a largely emission-free catalyst base material can be produced in simple manner.

To solve this problem, the subject matter of the invention is a method for producing catalytically active layered silicates, especially nanoscale composite layered silicates, with one or more intercalated layers, especially Al-pillared and/or Ti-pillared clays, wherein a metal solution, preferably polycationic metal solution, is added to the layered silicate and then the mixture is dried to generate the metal atom pillars that support the respective intercalated layer, wherein a metal salt, especially transition metal salt, is further added to the dry substance obtained in such a way to generate a dry mixture, and wherein the dry mixture is finally heated, preferably to values of higher than 300°C, so that the metal atoms or transition metal atoms become included in the intercalated layer with evolution of gas and the dry mixture is simultaneously calcined.

The catalytically active layers silicates are usually nanoscale composite layered silicates, or in other words layered silicates in which the described solid-state ion exchange or inclusion of the metal atoms or transition metal atoms takes place in the nanometer range. The same is true for the formation of the metal atom pillars supporting the respective intercalated layer. In this category there fall mainly metal oxides or metal polyoxides, which in principle mean metal compounds (containing oxygen) that ensure the supporting effect by the formation of pillars in the respective intercalated layer.

In order now to produce this intercalated layer, the metal solution or polycationic metal solution or metal ion complex solution in question is added to the layered silicate and then the mixture is dried, calcined and if necessary converted to ammonium form to generate the pillars supporting the respective intercalated layer. This is usually carried out in alkaline solution, in which case sodium hydroxide solution is mostly used to prepare the metal solution.

In the described wet-chemical modification of the layered silicate, the sodium hydroxide or aluminium hydroxide previously present in solution precipitates out, and the metal ions or metal complex ions are deposited in the intercalated layers or become attached to the surfaces of the layered silicates. In the intercalated layer they form pillars in the nanometer range after drying. Hereby the intercalated layers or interstices between the silicate layers not only are

## Claims:

1. A method for producing catalytically active layered silicates, with one or more intercalated layers,
  - wherein a metal solution is added to the layered silicate (3.1) and then the mixture is dried to generate the metal atom pillars that support the respective intercalated layer (4.1),
  - wherein a metal salt is further added to the dry substance obtained in such a way to generate a dry mixture (5.1), and
  - wherein the dry mixture is finally heated, so that the metal atoms or transition metal atoms become included in the intercalated layer (6.1) and the dry mixture is simultaneously calcined.
2. A method according to claim 1, characterized in that an Al, Ti, Fe, Cu, Cr solution or a polyoxide mixture of these or similar metals is used as the metal solution.
3. A method according to claim 1 or 2, characterized in that the dry mixture is heated to values of higher than 300°C, especially between 450°C and 700°C.
4. A method according to one of claims 1 to 3, characterized in that the mixture of layered silicate and metal solution is first washed, then filtered and only thereafter heated slowly, whereupon the reaction of formation of the metal atom pillars takes place spontaneously at room temperature.
5. A method according to claim 4, characterized in that, following the described drying step, the substance is shock-heated, in order to achieve a homogeneous distribution of the dehydrated metal atom pillars in the intercalated layers.

6. A method according to claim 5, characterized in that the temperature gradient for the shock-heating step is adjusted such that a temperature rise of about 100°C or even greater per 10 minutes is achieved, the temperature being raised, for example from 100°C to 500°C in 30 minutes.
7. A method according to one of claims 1 to 6, characterized in that, after formation of the metal atom pillars in the intercalated layers, the layered silicate is processed by an acid treatment to a cationic condition or by an alkaline treatment to an anionic condition, then is washed and dried.
8. A method according to one of claims 1 to 7, characterized in that the metal salt or transition metal salt is formed as a salt based on transition metals such as copper, titanium, indium, cerium, lanthanum or the like.
9. A method according to claim 8, characterized in that the metal salt is copper nitrate or copper sulfate.
10. A method according to one of claims 1 to 9, characterized in that the substance resulting from the dry mixture is shaped, for example in the course of an extrusion operation, if necessary with addition of a binder, such as aluminum oxide.
11. A method according to claim 10, characterized in that the extruded product obtained in this way is dried.
12. A method according to one of claims 1 to 11, characterized in that a two-layer and/or three-layer mineral is used as the layered silicate.

13. A method according to one of claims 1 to 12, characterized in that the internal surface of the produced layered silicate has values of approximately 300 m<sup>2</sup>/g and larger.

14. A method according to one of claims 1 to 13, characterized in that the catalytically active layered silicates are nanoscale composite layered silicates, especially Al-pillared and/or Ti-pillared clays.

15. A method according to one of claims 1 to 14, characterized in that the metal solution is a polycationic metal solution.

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